

Poster Sessions

Ultra-high porosity in MOFs: One of the most important properties of metal-organic frameworks (MOFs) is their high porosity and high specific surface area, which has led to many applications concerned with gas storage, separations, and catalysis. An important consideration in maximizing the uptake of gases within porous MOF crystals is to increase the number of adsorptive sites within a given material. We have succeeded in preparing materials with ultra high porosity (10400 m²/g Langmuir) by combining octahedral SBUs with tritopic linkers, following the isoreticular expansion principle (MOF-180, -200). In addition, the combination of tritopic and ditopic linkers also led us to highly porous materials with new topologies (MOF-210, -205).

Multiple Functional Groups of Varying Ratios in Metal-Organic Frameworks (MTV-MOFs): We show that MOFs can incorporate a large number of different functionalities on linking groups in a way that mixes the linker, rather than forming separate domains. Our strategy to making MTV-MOFs is to assemble their structures from links with different functional groups whose orientation, number, relative position, and ratio along the backbone can be controlled by virtue of the unchanged length of the link and its unaltered connectivity. In this way, each of the pores within the MOF would have an array of functionalities pointing into its center.

Porous Materials with charge mobility and electrical conductivity:

We have prepared two covalent organic frameworks (COFs) with structures based on covalently linked porphyrin units to afford sheets in which the porphyrin units are stacked laterally to give an efficient conducting interface. The two porphyrin COFs (COF-66 and COF-366) have been found to be hole conducting with mobilities as high as 8.1 and 3.0 cm²V⁻¹s⁻¹. Such multifunctional conducting COFs combine thermal stability, electrical conductivity, high charge mobility, and pore accessibility and, as the first members of the COF family to exhibit such properties, represent an important step towards plastic electronics and optoelectronics.

By combining 1,2,3-triazole and divalent metal atoms, a new family of seven metal-triazolates, METs, has been prepared. The crystal structure of the compounds has been determined *ab initio* by applying the charge flipping method to powder X-ray diffraction data obtained from a laboratory X-ray source. The new compounds exhibit a dia network type, built up from tetrahedral secondary building units. All the materials are porous, having surface area in the range 480 - 1100 m²/g. The Fe(II)-MET material has proven to have electrical conductivity. Measurements carried out in a pressed pellet of Fe-MET reveals a conductivity value of 10⁻³ S cm⁻¹.

Keywords: porous, powder, MOFs

MS24.P56

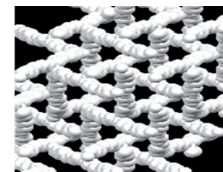
Acta Cryst. (2011) A67, C378

A series of rarely observed all helical 3-D coordination polymers derived from various chiral amino acids :effect of amino acid side chain & their unique ability of separating cations & anions

Subhabrata Banerjee, Parthasarathi Dastidar, *Department of organic chemistry, Indian association for the cultivation of science, jadavpur, Kolkata (India)*. E-mail:ocsb@iacs.res.in

Design and synthesis of functional MOF is an active area of material research for their various potential applications viz. molecular storage, catalysis, magnetism, non-linear optical material, selective anion separation etc. Crystal engineering is a major support in developing different novel functional MOFs.[1] When these tailor-made MOFs engineered by crystal engineering approach are chiral then these become even more important for their immense possibility to be used as a promising functional material. Moreover chiral helical coordination polymers are also interesting for their fascinating supramolecular architectures. Four rarely observed all

helical 3-D coordination polymers (all belong to enantiomorphic P3₂1 space group) derived from chiral amino acid based viz. Phenyl alanine, alanine, leucine bis pyridyl bis amide ligands with Cu⁺² are studied by single crystal X-ray diffraction. The study is undertaken in order to demonstrate the effect of amino acid side chain on overall supramolecular architecture. This is a part of our ongoing research efforts which include a detail and systematic study of amino acid side chain on overall supramolecular architecture within a coordination network[2]. The unique ability of those MOF to separate cations and anions are also worthwhile to be mentioned here.



General views of MOFs along c-direction

[1] (a) D. Bradshaw, J.B. Claridge, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273-282; (b) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305-326; (c) D. Sun, Y. Ke, D. J. Collins, G.A. Lorigan, H.C. Zhou, *Inorg. Chem.* **2007**, *46*, 2725-2724; (d) E.Q. Gao, Y.F. Yue, S.Q. Bai, Z. He, C.H. Yan, *J. Am. Chem. Soc.* **2004**, *126*, 1419-1429; (e) C.D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940-8941; (f) Y. Liu, X. Xu, F. Zheng, Y. Cui, *Angew. Chem. Int. Ed.* **2008**, *47*, 4538-4541; (g) R.K. Feller and A.K. Cheetham, *Dalton Trans.*, **2008**, 2034-2042; (h) S.T. Wu, Y.R. Wu, Q.Q. Kang, L-S Zheng, *Angew. Chem. Int. Ed.* **2007**, *46*, 8475-8479. [2] S. Banerjee, N.N. Adarsh, P. Dastidar, *CrystEngComm.* **2009**, *11*, 796-802.

Keywords: 3D, coordination, polymer

MS24.P57

Acta Cryst. (2011) A67, C378

Photonic materials: how protonation influence structure and properties

Tatiana V. Timofeeva,^a Alexandr Fonari,^a Tiffany L. Kinnibrugh,^a Evgeniya S. Leonova,^b Irina L. Odinets,^b Mikhail Yu. Antipin,^{a,b} ^a*Department of Biology and Chemistry, New Mexico Highlands University, Las Vegas, NM, (USA)*. ^b*Institute of Organoelement Compounds, RAS, Moscow, (Russia)*. E-mail: tvtimofeeva@nmhu.edu

Salt formation is the most common and effective method to increase solubility and dissolution rates of drugs. For compounds containing amino groups their protonation in presence of acids leads to formation of salts with better solubility than for neutral compounds. On the other hand, if consider compounds for potential application as photonic materials in photodynamic therapy, it should be taken into account that protonation might significantly influence molecular polarizability, and hence photonic properties of such materials. Series of neutral, mono- and triprotonated (dialkylammonio)-benzylidenepiperidones was structurally characterized and geometrical characteristics were compared with results of quantum-chemical computations. Spectroscopic evaluation of one and two-photon absorption properties, and hyperpolarizabilities values are compared with geometrical characteristics obtained for neutral and protonated materials.

Keywords: organic salts, NLO properties, benzylidenepiperidones

MS24.P58

Acta Cryst. (2011) A67, C378-C379

Two Co(III) dioximates with unprecedented V-shape ligands in apical positions

Paulina Bourosh,^a Ion Bulhac,^b Maria Cocu,^b Eduard Coropceanu,^b

Olga Ciobanica,^b Victoria Gutium,^b Janusz Lipkowski,^c ^a*Institute of Applied Physics, Academy of Sciences of R. Moldova, Academy str., 5, MD2028, Chisinau, (Moldova); Tel.: + 373 22 738154; fax: 373 22 725887.* ^b*Institute of Chemistry, Academy of Sciences of R. Moldova, Academy str., 3, MD2028, Chisinau, (Moldova).* ^c*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01 224 Warszawa, (Poland).* E-mail: bourosh.xray@phys.asm.md

Condensation of isonicotinic hydrazide and acetylacetone resulted in the formation of novel V-shape organic ligand (L) that consists of a six-membered pyridine and five-membered hydroxyl, dimethyl-substituted diazole cycles joined *via* carbonyl bridge [1]. The metathesis reaction between [Co(DfgH)₂Br(H₂O)] (DfgH₂=diphenylglyoxime) and L resulted in mononuclear octahedral complex [Co(DfgH)₂BrL] (1) with the substitution of water molecule in apical position by L ligand (Fig. 1). The dihedral angle between the cycle units is equal 49.5° in L in 1. The reaction starting from [Co(DmgH)₂Cl(H₂O)] (DmgH=dimethylglyoxime) and L resulted in the mononuclear octahedral Co(III) complex again with the composition [Co(DmgH)₂ClL'] (2), were unexpectedly L' represent the dehydrated derivative of L (Fig. 2). The dihedral angle between pyridine and diazole rings is equal 88.8° in L' in 2. While the organic molecules L/L' have several donor centers, both ligands act as monodentate ligands and coordinate with metal atom by nitrogen atom of pyridine fragment.

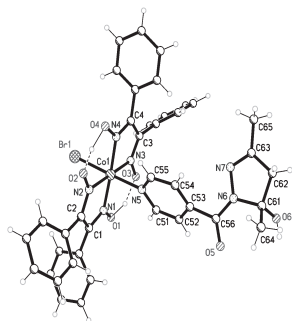


Fig. 1. The structure of [Co(DfgH)₂BrL] (1)
Co-N1 1.881(3) Å
Co-N2 1.890(3) Å
Co-N3 1.889(3) Å
Co-N4 1.893(3) Å
Co-N5 1.980(3) Å
Co-Br 2.3768(7) Å

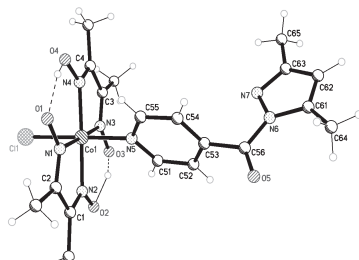


Fig. 2. The structure of [Co(DmgH)₂ClL'] (2)
Co-N1 1.884(2) Å
Co-N2 1.890(2) Å
Co-N3 1.904(2) Å
Co-N4 1.917(2) Å
Co-N5 1.969(2) Å
Co-Cl 2.2320(7) Å

Explanation of the different structure of L and L' in the complex requires further research.

Acknowledgements: This work was supported by the 10.819.05.03F project.

[1] M. Cocu, S. Shova, V. Gutium, I. Bulhac. *The 5th International Conference on Materials Science and Condensed Matter Physics*. September, 13 - 17, 2010, Chisinau, Republic of Moldova, MSP 11P, p. 80.

Keywords: cobalt(III), coordination compound, X-ray

MS24.P59

Acta Cryst. (2011) A67, C379

Influence of ligand substituent on molecular architecture; Very large changes in structural assembly and coordination geometry
Hamid Reza Khavasi, Maryam Mehdizadeh, Mahmood Azizpoor Fard. *Department of Chemistry, Shahid Beheshti University, G.C.,*

Evin, Tehran 1983963113 (Iran). E-mail: h-khavasi@sbu.ac.ir

The planning in coordination crystal engineering, construction of the structures of crystalline coordination compounds, [1] depends on a number of experimental variables such as the solvent, time of reaction, reagent ratio, temperature, pH, guest molecules and counterions. In this regard, chemical structure of the organic ligand [2] -eventh slight of the substitute position- and preferred coordination geometry of the metal [3] play an important role on the formation of different molecular architecture of complexes in the assembly processes. To make progress in controlling specific interactions in the solid state of coordination compounds requires systematic investigations of the effects of different factors on the final structures. Despite to the potential utility, from crystal engineering point of view, there has been little attention to systematic studies that examine the effect of the substituent variation of the ligand on the supramolecular aggregation of coordination complexes.

In this study, *N*-(aryl)-2-pyrazinecarboxamide ligands with two different aryl groups (o-anisidyl, L1, and o-phenitidyl, L2, groups) have been employed for the synthesis of six Hg (II) complexes, [HgCl₂(L1)₂]_n, [HgBr₂(L1)₂]_n, [HgI₂(L1)₂]_n, [Hg₃Cl₆(L2)₃·HgCl₂(L2)], [HgBr₂(L2)] and [HgI₂(L2)] in order to get insights to the substituent effects on the molecular architecture of complexes. Structural analysis of mercury (II) halides containing L1 ligand demonstrated that the assembly process produced infinite 2D structures. For mercury (II) halides containing L2 ligand, the assembly processes are involved weak interaction between monomeric Hg(II) coordination compounds.

[1] (a) F. Grepioni, D. Braga, *Wiley-VCH: Weinheim, Germany* 2007, (b) G.R. Desiraju, *Elsevier: Amsterdam*, 1989. [2] (a) Y.T. Wang, H.H. Fan, H.Z. Wang, X.M. Chen, *Inorg. Chem.* 2005, 44, 4148-4150, (b) C.N.R. Rao, S. Natarajan, R. Vaidyanathan, *Angew. Chem. Int. Ed.* 2004, 43, 1466-1496. [3] L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato, *New J. Chem.* 2003, 27, 483-489, (b) T. Burchell, R.J. Puddaphatt, *Inorg. Chem.* 2005, 44, 3718-3730.

Keywords: carboxamide, mercury, crystal engineering

MS24.P60

Acta Cryst. (2011) A67, C379-C380

New supramolecular dimer and 2D-supramolecular layers formation through hydrogen bonds

Jan Moncol, Michaela Stolickova, Jana Medvecká, Dušan Valigura, *Institute of Inorganic Chemistry, FCHPT, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, (Slovakia).* E-mail: jan.moncol@stuba.sk

Coordination compounds with both donor A-H and acceptor B groups and forming hydrogen bonds are used as building block for construction of supramolecular networks. Some copper(II) carboxylate complexes have shown that the intermolecular H-bonds can alter their magnetic properties. We have recently published mononuclear molecular complex [1], binuclear molecular complex [2] and more coordination polymers [3,4] which exhibit similar magnetic properties. These very similar magnetic properties of mononuclear, binuclear as well as polymeric complexes could be explained by the presence of very similar H-bond systems, supramolecular synthons, that are pathway for antiferromagnetic interactions.

In this report we present new supramolecular dimer [Cu(3-Brbz)₂(dena)(H₂O)₂] (3-Brbz is 3-brombenzoate, dena is *N,N*-diethylnicotinamide as terminal ligand) and series of 1D-coordination polymers of general formula [Cu(RCO₂)₂(μ-dena)(H₂O)]_n (RCO₂ are 3-chlorbenzoate, 4-chlorbenzoate or 3,5-dichlorbenzoate, and dena as bridging ligand) with similar system of hydrogen bonds and properties. The hydrogen bonds described by R₂²(10) and R₂²(12) supramolecular